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AMAT Docket No. 2616 US/RTP/LE  
BSTZ Docket No. 004887.P090

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

Guangcai Xing, et al.

Application No. 09/298,064

Filed: April 22, 1999

For: APPARATUS AND METHOD FOR  
EXPOSING A SUBSTRATE TO PLASMA  
RADICALS

Examiner: Rudy Zervigon

Art Unit: 1763

**APPEAL BRIEF**

Mail Stop Appeal Brief - Patents  
Commissioner for Patents  
P. O. 1450  
Alexandria, VA 22313-1450

Dear Commissioner:

Applicant submits, in triplicate, the following Appeal Brief pursuant to 37 C.F.R. § 1.192 for consideration by the Board of Patent Appeals and Interferences. Applicant also submits herewith a check in the amount of \$330.00 to cover the cost of filing the opening brief as required by 37 C.F.R. § 1.17(c). Please charge any additional amount due or credit any overpayment to deposit Account No. 02-2666.

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## **I. REAL PARTY IN INTEREST**

Guangcai Xing, Gary E. Miner, David R. Lopes, Sita R. Kaluri, and Richard N. Tauber, the parties named in the caption, assigned their rights to that disclosed in the subject application through an assignment recorded on July 2, 1999 (10063/0939 and 10063/0945) to Applied Materials, Inc. of Santa Clara, California. Thus, as the owner at the time the brief is being filed, Applied Materials, Inc. of Santa Clara, California is the real party in interest.

## **II. RELATED APPEALS AND INTERFERENCES**

There are no other appeals or interferences known to Applicants, Applicants' legal representative, or Applicants' assignee that will directly affect, or be directly affected by, or have a bearing on the Board's decision in the pending appeal.

## **III. STATUS OF CLAIMS**

Claims 1-7 and 17-20 are pending in the application. Claim 19 has been canceled. All pending claims are rejected.

## **IV. STATUS OF AMENDMENTS**

The amendment submitted on May 8, 2003, amending claims 1, 6, 17 and 20 has been entered.

## **V. SUMMARY**

Various embodiments to the claims relate to an apparatus, a system, and a machine readable storage medium suitable for use in film formation processing. Representatively, an apparatus includes a first reaction chamber and a gas source coupled to the first reaction chamber to supply a nitrogen gas to the first reaction chamber. An excitation energy source is coupled to the first reaction chamber to generate a nitrogen plasma comprising nitrogen ions and radicals from the nitrogen gas. The first reaction chamber is coupled to a second reaction chamber. The second reaction chamber is adapted to house a substrate for film formation at a site in the second reaction chamber. The first reaction chamber is separated from the substrate site by distance equivalent to the lifetime of nitrogen ions at a plasma generation rate such that nitrogen radicals react with the substrate in a film conversion step.

In terms of a circuit device application, the apparatus may be used, for example, to modify a film on a substrate such as a film on a semiconductor wafer. As described in the application at Figures 1 and 2 and the accompanying text, a substrate including a silicon dioxide film on surface thereof may be present in the second reaction chamber. The silicon dioxide film may then be exposed to a nitrogen environment delivered from the first reaction chamber. The nitrogen

environment is a plasma created by the excitation energy source coupled to the first reaction chamber. Due to the separation between the first reaction chamber and the second reaction chamber, the plasma is free of nitrogen ions leaving nitrogen radicals to react with the substrate in a film conversion step, e.g., converting silicon dioxide to a nitrogen containing material such as  $\text{Si}_3\text{N}_4$  and  $\text{Si}_x\text{O}_y\text{N}_z$  material.

In another embodiment of the claims, an apparatus for exposing a substrate to plasma is described. The apparatus includes a first reaction chamber and means for supplying a nitrogen gas to the first reaction chamber. The apparatus also includes means for generating a plasma from the nitrogen gas, the plasma comprising ions and radicals. The apparatus further includes a second reaction chamber having means for housing a substrate for film formation processing. Finally, the apparatus comprises means for providing the plasma to the second reaction chamber substantially free of nitrogen ions such that the nitrogen radicals react with a substrate in a process conversion step.

In another embodiment of the claims, a system for reacting a plasma with a substrate is disclosed. The system includes a first chamber, a nitrogen gas source coupled to the first chamber, an energy source coupled to the first chamber, and a second chamber configured to house a substrate for film formation processing. The system also includes a system controller configured to control the introduction of a nitrogen gas from the nitrogen gas source into the first chamber and to control the introduction of an energy from the energy source. A memory is also included. The memory is coupled to the controller and includes a computer readable medium having a computer readable program embodied therein for directing operation of the system. The computer readable program includes instructions for controlling a nitrogen gas source and the energy source to convert a portion of a nitrogen gas supplied by the gas source into a plasma comprising nitrogen ions and radicals. The first reaction chamber is separated from the second reaction chamber by distance equivalent to the lifetime of the nitrogen ions at a plasma generation rate such that the radicals react with a substrate in the second chamber in a film conversion step.

In another embodiment of the claims, a machine readable storage medium containing executable program instructions is described. The program instructions, when executed, cause a digital processing system to perform a method of reacting a plasma with a substrate. The method includes generating a plasma from nitrogen comprising radicals and nitrogen ions in a first chamber and transferring the plasma radicals via a distance equivalent to the lifetime of the nitrogen ions into a second chamber substantially free of ions.

## VI. ISSUES

The issues involved in this appeal are as follows:

1. Whether claims 1-4 and 6-7 are anticipated under 35 U.S.C. §102(b) by "Role of N<sub>2</sub> Addition on CF<sub>4</sub>/O<sub>2</sub> Remote Plasma Chemical Dry Etching of Polycrystalline Silicon," Matuso, et al. (Matsuo).
2. Whether claims 1-4 and 6-7 are obvious under 35 U.S.C. §103(a) over Matsuo.
3. Whether claims 17-20 are anticipated under 35 U.S.C. §102(b) by U.S. Patent No. 5,082,517 issued to Moslehi (Moslehi).
4. Whether claim 5 is obvious under 35 U.S.C. §103(a) over Matsuo in view of U.S. Patent No. 6,130,118 issued to Yamazaki et al. (Yamazaki).

## VII. GROUPING OF CLAIMS

Applicant groups the claims as follows:

- Group I - Claims 1-4;
- Group II - Claim 5;
- Group III - Claims 6-7;
- Group IV - Claims 17-18; and
- Group V - Claims 20.

The reason for the independent patentability of the separate groups is discussed in detail below.

## VIII. ARGUMENTS

### A. Overview of Cited References

#### 1. Overview of Matsuo

Matsuo describes experimental etching procedures, specifically, chemical dry etching of silicon. Matsuo generates a microwave plasma in a plasma applicator coupled to a processing chamber for an etch process. As part of the experimental etching procedures, the plasma is separated from the processing chamber by tubing of various lengths (0 to 125 centimeters). Matsuo describes etching silicon in a CF<sub>4</sub> plasma with oxygen (O<sub>2</sub>) and/or nitrogen (N<sub>2</sub>) addition. Matsuo describes that no separation achieves better etching results than a separation of the plasma from the processing chamber.

Matsuo describes experimental etching procedures, not film formation procedure. Matsuo describes the etching process as generating a "reaction layer" but does not describe the reaction layer as containing any nitrogen constituents. Further, since Matsuo is concerned with removing silicon, the reaction layer presumably is transient — i.e., present only to the extent and duration that silicon is removed during a chemical reaction.

## **2. Overview of Yamazaki**

Yamazaki describes a plasma reaction apparatus suitable for depositing a film. In an embodiment cited by the Patent Office, a multiobjective deposition is described. That system includes preliminary chambers 101 and 106; process chamber 104 for rapid thermal anneal processes; deposition process chamber 103; and deposition chamber 105. Process chamber 104 is for performing rapid thermal anneal processes. In the embodiment described, an aluminum nitride film is formed in deposition chamber 103 and the substrate containing the aluminum nitride film is transported to anneal chamber 104. Rapid thermal anneal by irradiation of infrared light is performed in process chamber 104. The substrate is then transported to processing chamber 106 where a silicon oxide film is deposited. Once the silicon oxide film is deposited, the substrate is transferred again to processing chamber 104 for a rapid thermal annealing process. The substrate is then transferred to deposition chamber 105 where a silicon film is deposited. As described in the example, processing chamber 104 is not used as a deposition chamber.

## **3. Overview of Moslehi**

Moslehi describes a system for controlling plasma density in the context of deposition, etching, and cleaning by remotely locating a plasma source from a process chamber. In one embodiment, a system controller serves as a plasma density controller that variably controls properties associated with fabrication process plasma medium for semiconductor wafer processing. These properties include the concentration of activated ions and neutral species in plasma. In this context, Moslehi describes deposition and etching. Moslehi does not describe film conversion.

### **B. Group I: Rejection of Claims 1-4 under 35 U.S.C. §§102(b) or 103(a)**

The Patent Office rejects claims 1-4 under 35 U.S.C. §102(b) as anticipated by Matsuo. Independent claim 1 describes an apparatus including a first reaction chamber, a gas source coupled to the first reaction chamber to supply nitrogen gas to the first reaction chamber, and an excitation energy source coupled to the first reaction chamber to generate a nitrogen plasma comprising nitrogen ions and radicals from the nitrogen gas. The apparatus also includes a second reaction chamber adapted to house a substrate for film formation at a site in the second reaction chamber. The first reaction chamber is coupled to the second reaction chamber and separated from the substrate site by distance equivalent to the lifetime of the nitrogen ions at a plasma generation rate such that the radicals react to the substrate in the film conversion step.

Independent claim 1 is not anticipated by and is prima facie not obvious over Matsuo, because Matsuo does not describe:

- 1) a second reaction chamber adapted to house a substrate for film formation;

Matsuo describes only etching of silicon. The Patent Office references page 1805 of Matsuo describing a "reaction layer." A representative reaction layer is a  $\text{SiF}_x\text{O}_y$  reaction layer. Certainly, it is clear that in the removal of silicon during a silicon etch process, a reaction layer such as a  $\text{SiF}_x\text{O}_y$  reaction layer is only transient and is not a desired resulting film from an etch process. Accordingly, Matsuo cannot be read to describe a chamber adapted to house a substrate for film formation at a site in the chamber;

2) the first reaction chamber is coupled to the second reaction chamber and separated by a distance equivalent to the lifetime of nitrogen ions at a plasma generation rate.

Figure 4 of Matsuo (shown below) shows the polycrystalline silicon etch rate versus a quartz-lined transport tube (an "applicator") between the plasma and the etch chamber. The inverted triangle in each case represents nitrogen addition to an etch chemistry of  $\text{CF}_4$  or  $\text{O}_2/\text{CF}_4$  to etch polycrystalline silicon. As clearly evident by each figure, where nitrogen is added, the etch rate is best at zero separation. The teaching of Figure 4 is that, with respect to etching, if nitrogen is to be used, there should be no separation between the applicator (plasma generator) and the etch chamber.

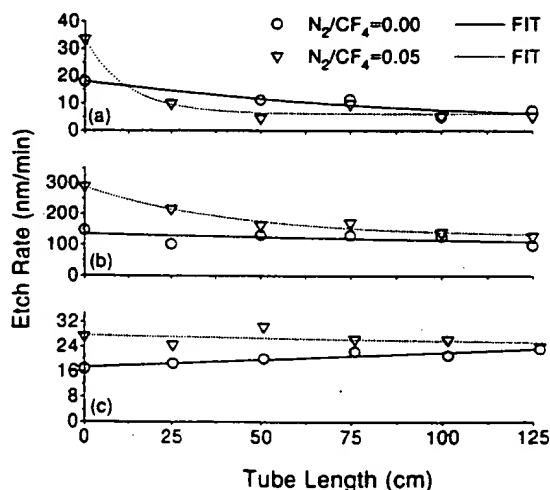


FIG. 4. Poly-Si etch rate vs quartz lined transport tube length. Panel (a) represents an  $\text{O}_2/\text{CF}_4$  ratio of 0.00, (b) 0.15, and (c) 0.75.

With respect to pending claim, the separation of the first reaction chamber from the second reaction chamber of a distance equivalent to a lifetime of the nitrogen ions at a plasma generation rate is a structural limitation of the claims. If, for example, the distance was less than the lifetime of the nitrogen ions, the nitrogen ions would presumably be available to possibly react with a substrate in a film conversion step. In addition, the description of the second reaction chamber as a chamber to house a substrate for film formation is a structural limitation identifying a class of chambers.



In terms of obviousness, the Patent Office states that "[m]otivation for Matsuo to optimize the operation of the apparatus to provide a separation between chambers such that the separation is equivalent to the lifetime of the nitrogen ion so that plasma's generation rate such that the radicals react with the substrate is to form a desired film." See paper no. 29, at 5. Applicants can find no such motivation. First, Matsuo is not concerned with forming a film; Matsuo is removing silicon. Second, Applicants remind the Patent Office that the mere fact that a reference or references might be combined or modified does not render the resulting combination obvious unless the prior art also suggest the desirability of the combination. MPEP Section 2143.01. In this case, clearly Matsuo does not teach separating an applicator and an etch chamber when nitrogen addition is contemplated. Instead, Matsuo teaches the exact opposite.

As noted above, Matsuo describes only etching of silicon. Matsuo does describe the formation of a reaction layer (e.g., an  $\text{SiO}_x\text{F}_y$  reaction layer), but Matsuo does not describe nitrogen (either plasma or ion) specifically being incorporated into a reaction layer or reacting with a substrate in a film conversion step.

Strong surface chemical changes are observed upon  $\text{N}_2$  addition, although little nitrogen is incorporated in the reaction layer. The nitrogen is active only as a reactive intermediate. Depending on the  $\text{O}_2/\text{CF}_4$  ratio, i.e., the predominance of F or O, either thinning or thickness growth of the modified surface layer can be seen.

Matsuo, page 1813 (does not say nitrogen is incorporated in a reaction layer or that nitrogen radicals react with a substrate in a film conversion step).

Even though nitrogen plays a profound role in the etching of silicon, it is not incorporated in a stable reaction layer.

Matsuo, page 1806 (does not say nitrogen is incorporated in a reaction layer or that nitrogen radicals react with a substrate in a film conversion step).

Matsuo at its core is directed to a known etching process of etching silicon with  $\text{CF}_4$ .  $\text{CF}_4$  is a common species for plasma etching with silicon and has been extensively studied. Applicants include herewith as Appendix B, a copy of relevant pages of "Silicon Processing for the VLSI Era, Volume 1: Process Technology," by S. Wolf and R.N. Taber (1986) (Wolf). Specifically, pages 547-551 titled "Etching Silicon and Silicon Dioxide in Fluorocarbon-Containing Plasmas" is provided. The authors of the cited treatise describe a  $\text{CF}_4$  plasma etching of silicon accomplished not by the  $\text{CF}_4$  molecules, but by radical species created by the disassociation of  $\text{CF}_4$  molecules; namely, fluorine atoms. See id. at 548. The products of the silicon-etching reaction are  $\text{SiF}_4$  and  $\text{SiF}_2$ . Id. The addition of oxygen ( $\text{O}_2$ ) to the  $\text{CF}_4$  feed of up to 20 percent by volume tends to increase the etching chemical reaction by increasing the fluorine concentration available for reaction with silicon. See id. at 549. Although the exact reason for this increase of fluorine species is

debated, there is no debate that it is still only fluorine (not oxygen and fluorine) that reacts with the silicon. See id.

Matsuo generally confirms the content of Appendix B. Matsuo additionally considers nitrogen's effect on the fluorine reaction with silicon. Matsuo does not ever say that nitrogen reacts with the silicon or is significantly present in a reaction layer for such reaction. Further, it cannot be assumed that nitrogen is present in the reaction layer because the reaction layer thickness might be increased with nitrogen addition to the  $CF_4$  feed. Referring again to the text in Appendix B, one theory for the increase in etch rate due to the presence of oxygen is that  $CF_3$  are absorbed on the silicon surface and the oxygen reacts with the carbon atom (not the silicon), leaving three fluorine atoms available for reaction with the silicon. See Wolf, page 549. Interpreting Matsuo, it is plausible that nitrogen's role is to also increase the fluorine's species (e.g., F,  $CF_2$ ,  $CF_3$ , etc.) available at the silicon surface to react with silicon and possibly increase a thickness of the reaction layer. It is noteworthy that, regardless of the species present, Matsuo is describing etching silicon. Certainly, it is not conceivable that the removal of silicon would result in a conversion of a film post-etching. Matsuo is removing material-silicon-by a chemical process involving the reaction of fluorine with silicon. Material is being removed not added.

For the above states reasons, claim 1 is not anticipated by and is not obvious over Matsuo. Claims 2-4 depend from claim 1 and therefore include all the limitations of that claim. For at least the reasons stated with respect to claim 1, claims 2-4 are not anticipated by and are not obvious over Matsuo.

### **C. Group II: Rejection of Claim 5 under 35 U.S.C. §103(a)**

Claim 5 is rejected under 35 U.S.C. §103(a) as obvious over Matsuo in view of in view of Yamazaki. Yamazaki is cited for describing a plasma reaction apparatus for film deposition.

Claim 5 depends from claim 1 and therefore contains all the limitations of that claim. Accordingly, claim 5 is not obvious over the cited references because the references do not disclose and provide any motivation for an apparatus including a first reaction chamber and a second reaction chamber having a substrate site separated from the first reaction chamber by a distance equivalent to the lifetime of nitrogen ions at a plasma generation rate. Further, there is simply no motivation to combine the teachings of Yamazaki, with respect to film deposition, with the teachings of Matsuo directed etching silicon. The references in fact relate to opposite teaching -- one deposition of film formation (Yamazaki), the other etching or material removal (Matsuo).

Applicants respectfully request that the Patent Office withdraw the rejection of claim 5 under 35 U.S.C. §103(a).

**D. Group III: Rejection of Claims 6-7 under 35 U.S.C. §§102(b) or 103(a)**

Independent claim 6 describes an apparatus including a first reaction chamber; means for supplying a nitrogen gas to the first reaction chamber; and means for generating a plasma from the nitrogen gas. The apparatus also includes a second reaction chamber having means for housing a substrate for film formation processing and means for providing the plasma to a second reaction chamber substantially free of nitrogen ions such that radicals from the plasma react with a substrate in a process conversion step.

Claim 6 is not anticipated by and is prima facie not obvious over Matsuo, because Matsuo does not describe, among other things, means for providing a plasma of nitrogen to a reaction chamber substantially free of nitrogen ions such that radicals react with a substrate housed for film formation in a process conversion step. There is no teaching in Matsuo that describes state of the nitrogen species once it is in the etch chamber. Presumably, the Patent Office cites tube length similar to those described in the Applicants' specification for teaching only radicals are present. As a preliminary matter, Matsuo favors a much shorter tube length distance when nitrogen is introduced. Second, there is no teaching in Matsuo that nitrogen radicals are available to react with a substrate.

The means for providing the radicals to the second reaction chamber in claim 6 is a structural limitation of the apparatus in that it at least establishes a relationship between the generated plasma and the second reaction chamber. Representatively, where a second reaction chamber is placed too close to a first chamber, nitrogen ions as well as radicals could be available to react with a substrate in the process conversion step.

In terms of the obviousness of claim 6 over Matsuo, Applicants again point to Figure 4 above in the discussion of Matsuo with respect to claim 1. The mere fact that Matsuo conducted experiments clearly show that no circulation between an applicator and an etch chamber is clearly optimal in the context of nitrogen use in etching silicon as opposed to a separation cannot render a claim that teaches a separation obvious since there is certainly no suggestion to separate the applicator and the etch chamber. See MPEP 2143.01.

Independent claim 6 is not anticipated by and is not obvious over Matsuo. Claim 7 depends from claim 6. For at least the reasons stated with respect to claim 6, claim 7 is not anticipated by and is not obvious over Matsuo.

**E. Group IV: Rejection of Claims 17-18 under 35 U.S.C. §102(b)**

The Patent Office rejects claims 17-18 under 35 U.S.C. §102(b) as anticipated by Moslehi.

Independent claim 17 relates to a system including a first chamber; a nitrogen source gas coupled to the first chamber; and an energy source coupled to the first chamber. The system also includes a second chamber configured to house a substrate for film formation processing and a

system controller configured to control the introduction of a gas from the gas source into the first chamber and to control the introduction of an energy from the energy source. The system also includes a memory coupled to the controller and instructions for controlling the gas source and the energy source to convert a portion of a nitrogen gas supplied by the gas source into a plasma. The first reaction chamber is separated from the second reaction chamber by a distance equivalent to the lifetime of nitrogen ions of a plasma generation rate such that radicals react with a substrate in the second chamber in a film conversion step.

Independent claim 17 is not anticipated by Moslehi, because Moslehi does not describe a system including a first reaction chamber and a second reaction chamber that are separated by distance equivalent to the lifetime of nitrogen ions at a plasma generation rate since that radicals react with a substrate in the second chamber in the film conversion step. Moslehi teaches preferably introducing both charged and neutral species to a process chamber. The Patent Office states that Moslehi teaches a plasma density controller to provoke controlling "the concentration" of activated ions and neutral species. This, however, is not a teaching anticipating a relationship between a plasma generation tube described in Moslehi and a process chamber (e.g., the distance between the plasma generation tube and a process chamber) equivalent to the lifetime of nitrogen ions. For the above stated reasons, claim 17 is not anticipated by Moslehi. Claim 18 depends from claim 17 and therefore contains all the limitations of that claim. For at least the reasons stated with respect to claim 17, claim 18 is not anticipated by Moslehi.

#### **F. Group V: Rejection of Claim 20 under 35 U.S.C. §102(b)**

The Patent Office rejects claim 20 under 35 U.S.C. §102(b) as anticipated by Moslehi.

Claim 20 relates to a machine-readable storage medium containing executable program instructions. When the program instructions are executed, the instructions cause a digital processing system to form a method of reacting a plasma with a substrate. The method includes generating a plasma from nitrogen comprising radicals and ions in the first chamber and transferring the plasma radicals via a distance equivalent to the lifetime of nitrogen ions into a second chamber substantially free of ions.

Independent claim 20 is not anticipated by Moslehi, because Moslehi does not describe a machine-readable storage medium containing program instructions including transferring plasma radicals of nitrogen via a distance equivalent to the lifetime of nitrogen ions into a chamber substantially free of ions. As noted above with respect to claim 17, Moslehi teaches introducing both charged and neutral species to a process chamber. Therefore, it cannot anticipate a claim including program instructions to deliver plasma radicals (e.g., neutral species) into a second chamber substantially free of ions. Applicants respectfully request that the Patent Office withdraw the rejection of claim 20 under 35 U.S.C. §102(b).

**IX. CONCLUSION AND RELIEF**

Based on the foregoing, Applicant requests that the Board overturn the rejection of all pending claims and hold that all of the claims of the present application are allowable.

Respectfully submitted,

BLAKELY, SOKOLOFF, TAYLOR & ZAFMAN

Date 3/22/04

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**CERTIFICATE OF MAILING:**

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Nedy Calderon 3/22/04  
Nedy Calderon Date

**X. APPENDIX A**

The claims involved in this Appeal are as follows:

1. (Previously Presented) An apparatus comprising:  
a first reaction chamber;  
a gas source coupled to the first reaction chamber to supply a nitrogen gas to the first reaction chamber;  
an excitation energy source coupled to the first reaction chamber to generate a nitrogen plasma comprising nitrogen ions and radicals from the nitrogen gas; and  
a second reaction chamber adapted to house a substrate for film formation at a site in the second reaction chamber,  
wherein the first reaction chamber is coupled to the second reaction chamber and separated from the substrate site by a distance equivalent to the lifetime of the nitrogen ions at a plasma generation rate such that the radicals react with the substrate in a film conversion step.
2. (Original) The apparatus of claim 1, wherein the excitation energy source supplies energy having a microwave frequency to generate a plasma from a gas.
3. (Original) The apparatus of claim 1, wherein the second reaction chamber is electrically non-biased.
4. (Original) The apparatus of claim 1, wherein the first reaction chamber is adapted to generate a nitrogen plasma, and the dimensions of the first reaction chamber are configured such that substantially all of the ions generated by the plasma are changed from an ionic state to a charge neutral state within the first reaction chamber.
5. (Original) The apparatus of claim 1, wherein the second reaction chamber is a rapid thermal processing chamber.
6. (Previously Presented) An apparatus for exposing a substrate to plasma, comprising:  
a first reaction chamber;  
means for supplying a nitrogen gas to the first reaction chamber;  
means for generating a plasma from the nitrogen gas, the plasma comprising ions and radicals;  
a second reaction chamber having means for housing a substrate for film formation processing; and

means for providing the plasma to the second reaction chamber substantially free of nitrogen ions such that the nitrogen radicals react with a substrate in a process conversion step.

7. (Original) The apparatus of claim 6, wherein the means for supplying a plasma comprises means for converting the gas to a plasma in the first reaction chamber.
8. (Withdrawn) A method of forming a plasma of radicals in a chamber, comprising:  
generating a plasma comprising ions and radicals in a first chamber;  
placing a substrate in a second chamber; and  
transferring the plasma into the second chamber to react with the substrate substantially free of ions.
9. (Withdrawn) The method of claim 8, wherein the substrate has a surface containing an oxide and the plasma is a nitrogen plasma, the method comprising:  
reacting the radicals with the oxide.
10. (Withdrawn) The method of claim 8, wherein prior to the step of transferring the radicals, the method further comprises the step of changing substantially all of the ions from an ionic stage to a neutral state.
11. (Withdrawn) A method of nitridizing an oxide, comprising:  
generating a plasma comprising ions and radicals in a first chamber;  
placing a substrate having an oxide layer on a surface in a second chamber;  
transferring the radicals of the plasma into the second chamber substantially free of ions;  
reacting a portion of the oxide layer and a portion of the plasma; and  
nitridizing a portion of the oxide layer of the substrate.
12. (Withdrawn) The method of claim 11, wherein the step of reacting the oxide and the plasma includes reacting the radicals with the oxide to form one of a silicon nitride molecule and a silicon oxynitride molecule.
13. (Withdrawn) The method of claim 11, wherein the step of nitridizing a portion of the oxide layer includes nitridizing an exposed surface of the oxide layer.
14. (Withdrawn) A method of forming a nitrogen containing material in the presence of an oxide, comprising:

generating a plasma comprising ions and radicals in a first chamber;  
placing a silicon wafer having an oxide in a second chamber;  
removing substantially all of the ions from the plasma;  
transferring the radicals of the plasma into the second chamber;  
reacting a portion of the oxide and a portion of the plasma; and  
forming a nitrogen containing material in a portion of the oxide layer of the substrate.

15. (Withdrawn) The method of claim 14, wherein the step of forming a nitrogen containing material includes forming one of a silicon nitride and a silicon oxynitride.

16. (Withdrawn) The method of claim 14, wherein the nitrogen containing material is formed in an exposed surface of the oxide layer.

17. (Previously Presented) A system for reacting a plasma with a substrate, comprising:  
a first chamber;  
a nitrogen gas source coupled to the first chamber comprising constituents adapted to react with a substrate;  
an energy source coupled to the first chamber;  
a second chamber configured to house a substrate for film formation processing;  
a system controller configured to control the introduction of a nitrogen gas from the nitrogen gas source into the first chamber and to control the introduction of an energy from the energy source; and  
a memory coupled to the controller comprising a computer-readable medium having a computer-readable program embodied therein for directing operation of the system, the computer-readable program comprising:  
instructions for controlling the nitrogen gas source and the energy source to convert a portion of a nitrogen gas supplied by the gas source into a plasma comprising nitrogen ions and radicals,

wherein the first reaction chamber is separated from the second reaction chamber by a distance equivalent to the lifetime of the nitrogen ions at a plasma generation rate such that the radicals react with a substrate in the second chamber in a film conversion step.

18. (Original) The system of claim 17, wherein the dimensions of the first chamber are configured such that substantially all of the ions generated in the plasma are changed from an ionic state to a charge neutral state in the first chamber.



19. (Cancelled)

20. (Previously Presented) A machine readable storage medium containing executable program instructions which when executed cause a digital processing system to perform a method of reacting a plasma with a substrate, comprising:

generating a plasma from nitrogen comprising radicals and nitrogen ions in a first chamber;  
and

transferring the plasma radicals via a distance equivalent to the lifetime of the nitrogen ions into a second chamber substantially free of ions.

**XI. APPENDIX B**

"Silicon Processing for the VLSI Era, Volume 1: Process Technology," by S. Wolf and R.N. Taber, pp. 547-551 (1986).

# SILICON PROCESSING FOR THE VLSI ERA

VOLUME 1:  
PROCESS TECHNOLOGY

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Published by:

**Lattice Press**

Post Office Box 340

Sunset Beach, California 90742, U.S.A.

Cover design by Roy Montibon and Donald Strout, Visionary Art Resources, Inc., Santa Ana, CA.

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**Library of Congress Cataloging in Publication Data**

Wolf, Stanley and Tauber, Richard N.

Silicon Processing for the VLSI Era

Volume 1 : Process Technology

Includes Index

1. Integrated circuits-Very large scale integration. 2. Silicon. I. Title

86-081923

ISBN 0-961672-3-7

9 8 7 6 5 4

PRINTED IN THE UNITED STATES OF AMERICA

involves the control of the large number of parameters that affect the process. Figure 5 illustrates some of the parameters that impact the gas-phase interactions, as well as the surface-plasma interactions. Although many macroscopic parameters can be controlled, such as the type of feed gas, power, and pressure, the precise effect of making any changes in these parameters is usually not well understood. In fact, a change in a single macroscopic parameter typically alters two or more basic *plasma* parameters, and possibly one or more of the surface parameters, such as temperature or electrical potential. This makes process development in plasma systems a challenge, and the use of factorial experimental design techniques for such tasks very useful<sup>9</sup> (see Chap. 18). In the introduction to the section on *Dry-Etch System Configurations*, a discussion is presented on how gas flow, pumping speed, and pressure are interrelated, and how this interrelationship is used to control pressure.

## ETCHING SILICON and SILICON DIOXIDE in FLUOROCARBON-CONTAINING PLASMAS

The etching of silicon and  $\text{SiO}_2$  in fluorocarbon plasmas is described in this section in substantial detail. This is done because these etching processes are very important in silicon VLSI fabrication. In addition, when the mechanisms of plasma etching were being first studied, the etching of silicon and  $\text{SiO}_2$  in plasmas containing  $\text{CF}_4$ , mixtures of  $\text{CF}_4 + \text{O}_2$ , and mixtures of  $\text{CF}_4 + \text{H}_2$ , yielded important data about many of the fundamental mechanisms that are operative in plasma etching, as well as information about the specific materials system under investigation. The conclusions from these studies led to the development of two models for organizing chemical and physical information on plasma etching. These models are the *fluorine-to-carbon ratio model* (or *F/C model*)<sup>10</sup>, and the *etchant-unsaturate model*<sup>11</sup>. Since the models are conceptually similar, although they emphasize different aspects of plasma etching, we describe only the F/C model. Details of the etchant-unsaturate model are given in Ref. 25.

We begin the discussion by considering several basic phenomena related to plasma etching processes. First, it is known that in the absence of a glow discharge, the gases commonly used in plasma etching do not react with the surfaces to be etched. For example,  $\text{CF}_4$  does not etch silicon without a discharge. This is due to the fact that  $\text{CF}_4$  does not chemisorb on Si, and thus

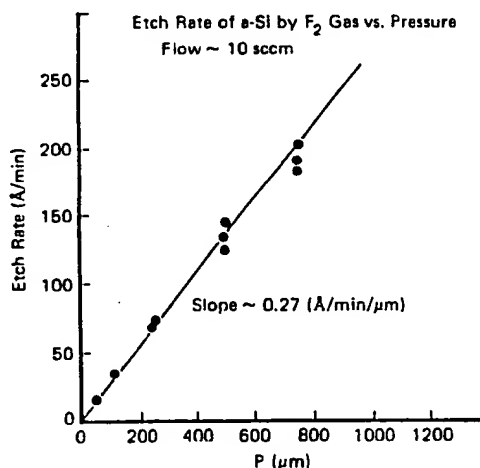


Fig. 6 The fluorine pressure dependence of the etch rate of amorphous silicon at room temperature<sup>12</sup>. Reprinted with permission of the publisher, the Electrochemical Society.

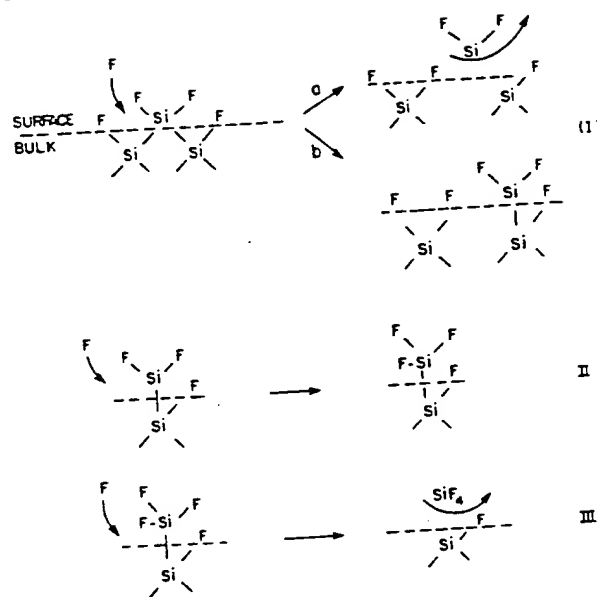


Fig. 7 Proposed mechanism for F-atom reaction with a silicon film leading to the products SiF<sub>2</sub> and SiF<sub>4</sub><sup>13</sup>. Reprinted with permission of the American Physical Society.

the step 3 of the dry-etching process described earlier does not occur. On the other hand, fluorine has been found to spontaneously etch Si, even without the presence of a discharge (Fig. 6)<sup>12</sup>. Thus, when a discharge of CF<sub>4</sub> is created, it is not the CF<sub>4</sub> molecules themselves that participate in the etching reaction. Instead, the etching is accomplished by the radical species which are created by the dissociation of CF<sub>4</sub> molecules; namely fluorine atoms. The products of the Si-etching reaction are SiF<sub>4</sub> and SiF<sub>2</sub>. A mechanism for the F-atom reaction with a Si film leading to gasification products has been proposed<sup>13</sup>, and is summarized in Fig. 7. The

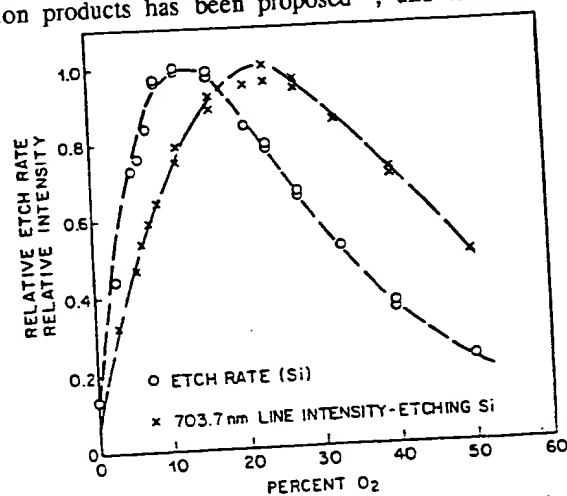


Fig. 8 The normalized etch rate for Si and the normalized intensity of the emission from electronically excited F atoms (703.7 nm line) versus the O<sub>2</sub> concentration in the CF<sub>4</sub>-O<sub>2</sub> etch gas<sup>4</sup>. Reprinted with permission of the American Physical Society.

steady-state surface seems to be a stable "SiF<sub>2</sub>-like" that must be penetrated by impinging F atoms in order for the SiF<sub>4</sub> to be formed. The etch rate of silicon (and SiO<sub>2</sub>) in pure CF<sub>4</sub>, however, is relatively low.

If small concentrations of O<sub>2</sub> are added to the CF<sub>4</sub> feed gas, however, the etch rates of both Si and SiO<sub>2</sub> are observed to dramatically increase (Fig. 8)<sup>14</sup>. The addition of the O<sub>2</sub> is also accompanied by an increase in the density of F-atoms in the discharge. Although several reasons have been advanced for this effect, it is certain that reactions between the oxygen atoms (or molecules) and the CF<sub>4</sub> molecules are responsible for the increased F-concentration. One of these reactions might be the gas phase oxidation of CF<sub>3</sub>, to first form COF<sub>2</sub> + F, which then dissociates into CO + F<sub>2</sub>. Another suggested reaction could involve CF<sub>3</sub> radicals that reach the silicon surface, and upon adsorption, contribute one C atom and 3 F-atoms to the surface. If an oxygen atom reacts with the adsorbed C atom, the 3 remaining F atoms are available to etch the Si. In any case, the etch rate of Si continues to increase until ~12% O<sub>2</sub> (by volume) is added. The etch rate of SiO<sub>2</sub> reaches its maximum value when ~20% O<sub>2</sub> is added. At greater concentrations, the additional O<sub>2</sub> dilutes the F concentration, and causes the etch rate to decrease. Figure 8 also shows that Si is etched much more rapidly than SiO<sub>2</sub> in CF<sub>4</sub>-O<sub>2</sub> plasmas, and thus high selectivity of Si over SiO<sub>2</sub> is in such plasmas is easy to obtain.

If H<sub>2</sub> is added to the CF<sub>4</sub> feed gas, the etch rate of silicon decreases monotonically to almost zero for H<sub>2</sub> additions ≥ 40%. The etch rate of SiO<sub>2</sub>, however, remains nearly constant for H<sub>2</sub> additions of up to 40% (Fig. 9)<sup>15</sup>. The silicon etch rate decrease occurs because the molecular hydrogen reacts with fluorine to form HF, and this drastically reduces the F atom concentration in the plasma. (It is said that the hydrogen scavenges F atoms). Although the effect of the Si etch rate decrease by itself may not be useful, the fact that the SiO<sub>2</sub> etch rate does not substantially decrease at the same time is valuable, because the SiO<sub>2</sub>-to-Si etch rate ratio increases. As a result, this allows a higher selectivity with respect to the substrate to be achieved when etching SiO<sub>2</sub> over Si. This selectivity is necessary when SiO<sub>2</sub> films must be etched down to an underlying Si layer, without significantly etching the Si.

The mechanism responsible for the high SiO<sub>2</sub>-to-Si etch rate selectivity involves the

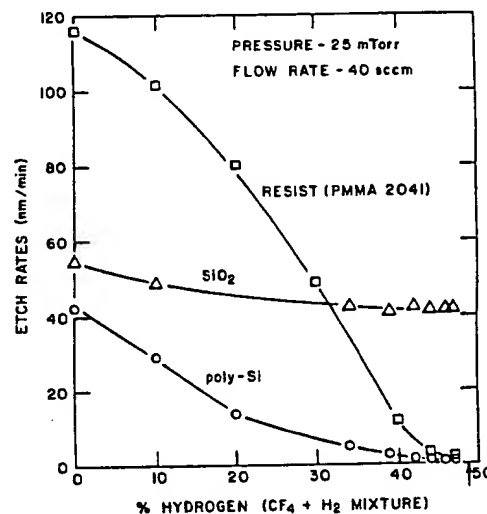


Fig. 9 The etch rate of Si, resist, and SiO<sub>2</sub> (measured in a reactive ion etching configuration) as a function of the concentrations of H<sub>2</sub> in the CF<sub>4</sub>-H<sub>2</sub> etch gas<sup>15</sup>. Reprinted with permission of the publisher, the Electrochemical Society.

combination of two phenomena: 1) the deposition of a nonvolatile residue; and b) the role of oxygen in the etching of  $\text{SiO}_2$ . If a nonvolatile layer (e.g. carbon residue) deposits on a surface during etching, and it is not removed, etching will cease. While such carbon residues are found to deposit on all surfaces inside an etch chamber containing  $\text{CF}_4\text{-H}_2$  plasmas, less accumulation is observed to occur on oxide surfaces than on non-oxide surfaces. There are several ways in which carbon can be deposited on a surface in fluorocarbon discharges. One way involves the dissociation of  $\text{CF}_3$ , or other fluorocarbon radicals, upon being chemisorbed on a surface. Less residue accumulates on  $\text{SiO}_2$  surfaces because some of the carbon combines with the oxygen in the  $\text{SiO}_2$  to form  $\text{CO}$  and  $\text{CO}_2$ , which are volatile. This in turn allows the  $\text{SiO}_2$  layer to continue to be etched under conditions when etching of the Si has ceased. Nevertheless, if the deposition rate of the carbon residue becomes too great, etching eventually stops on *all* surfaces in the chamber, including  $\text{SiO}_2$  surfaces. Other gases which also consume F atoms have been found to produce high  $\text{SiO}_2$ -to-Si selectivities<sup>16</sup> (even without the use of  $\text{H}_2$ ), including  $\text{CHF}_3$ ,  $\text{C}_3\text{F}_8$ , and  $\text{C}_2\text{F}_6$ . The reason for this effect is described as a part of the discussion on the *F/C ratio model*.

In practice, the exact process conditions that produce selective etching of  $\text{SiO}_2$  over Si are generally empirically derived for each reactor. This is due to the fact that high selectivity requires that the process be operated very close to the demarcation between etching and polymerization (where etching abruptly ceases). Although the adjustment of plasma conditions to achieve high  $\text{SiO}_2$ /Si selectivity remains an art, high selectivity is achievable. For example, selectivities of >20:1 at oxide etch rates of 600-1000 Å/min have been reported<sup>17</sup>.

#### Fluorine-to-Carbon Ratio Model

The *fluorine-to-carbon ratio (F/C) model*<sup>10</sup> is one of the two models which have been evolved to assist in assimilating the large amount of information on chemical and physical mechanisms observed in plasma etching. That is, the model represents an attempt to organize such information into a framework that allows processes to be developed more efficiently, by providing some basis for predicting the effects of various parametric variations. The F/C ratio is the ratio of the fluorine-to-carbon species, which are the two "active species" involved in the etching of Si and  $\text{SiO}_2$  (as well as other materials etchable in fluorocarbon plasmas, including  $\text{Si}_3\text{N}_4$ , Ti, and W). The F/C ratio model does not attempt to account for the specific chemistry taking place in the glow discharge, but instead treats the plasma as a ratio of F to C species which can interact with the Si or  $\text{SiO}_2$  surface. The generation or elimination of these "active species" by various mechanisms or gas additions then alters the initial F/C ratio of the inlet gas. Increasing the F/C ratio increases Si etch rates, and decreasing the F/C ratio lowers them.

For example, a pure  $\text{CF}_4$  feed gas has an F/C ratio equal to four. If the plasma environment causes Si etching, however, this phenomenon consumes F atoms without consuming any carbon, and thus the F/C ratio is reduced. If more Si surface is added to the etching environment, the F/C ratio is further decreased, and the etch rate is also reduced. The addition of  $\text{H}_2$  to the  $\text{CF}_4$  feed gas causes the formation of HF, but does not consume any carbon, thereby the F/C ratio and the etch rate are again reduced. Finally, the utilization of gases in which the F/C ratio is <4, such as  $\text{CHF}_3$  or  $\text{C}_3\text{F}_8$ , also has the effect of producing an F/C ratio smaller than that present in a plasma of pure  $\text{CF}_4$ . Their use is found to produce very similar effects in the etching chemistry as the other two procedures. Plasmas in which the F/C ratio is decreased to less than 4, are termed *fluorine-deficient plasmas*.

Conversely, the addition of  $\text{O}_2$  has the effect of *increasing* the F/C ratio, because the oxygen consumes more carbon (by forming  $\text{CO}$  or  $\text{CO}_2$ ), than F atoms (by the formation of  $\text{COF}_2$ ). Other feed gases that can be added to increase the F/C ratio include  $\text{CO}_2$ ,  $\text{F}_2$ , and  $\text{NO}_2$ .

The cause of the high selectivity of  $\text{SiO}_2$ -to-Si in  $\text{CF}_4 + \text{H}_2$  plasmas can be elucidated



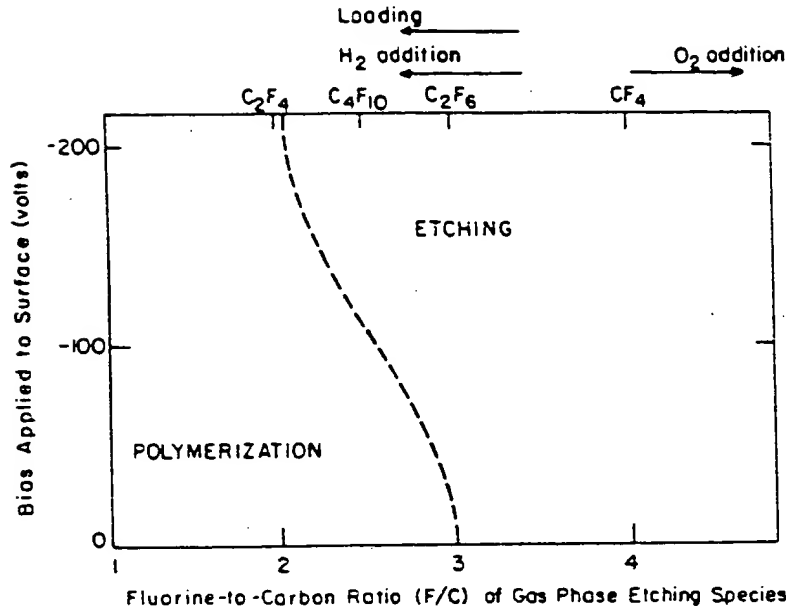


Fig. 10 Illustrative plot of the boundary between polymerizing and etching conditions as influenced by the fluorine-to-carbon ratio of the chemically reactive species and the bias applied to a surface in the discharge<sup>10</sup>. Reprinted with permission of the American Physical Society.

with the aid of the F/C ratio model. That is, even though the F/C ratio in such plasmas is less than 4, the  $\text{SiO}_2$  contributes oxygen (which consumes carbon), thus locally compensating for the decreased F/C ratio at the  $\text{SiO}_2$  surface<sup>19</sup>. As long as the F/C ratio at the oxide surface has a value close to that which exists in a pure  $\text{CF}_4$  plasma,  $\text{SiO}_2$  etching continues to proceed at the same rate. Meanwhile, since the F/C ratio at the Si surface is less than 4, the local etch rate decreases. To summarize, the F/C ratio model is useful for linking together the effects of a diverse set of phenomena, including the effects of many feed gases and  $\text{SiO}_2/\text{Si}$  selectivity.

The F/C ratio can also be used to qualitatively portray the demarcation between etching and polymerization as it varies according to changes in some process condition (Fig. 10). In this figure the boundary between polymerization (x-axis) is shown to vary as a bias voltage (y-axis) is applied to the substrate. The bias voltage has the effect of causing increased bombardment of the surface by energetic ions, which removes the nonvolatile residue layer by sputtering. This allows etching to occur at lower F/C ratios than if the carbonaceous polymer film were not simultaneously removed by sputtering and etching. This effect, as will be described in the following section, may be utilized as a technique to control sidewall profiles of etched layers.

## ANISOTROPIC ETCHING and CONTROL OF EDGE PROFILE

Up to this point in our discussion we have considered the etching of Si and  $\text{SiO}_2$  in fluorocarbon plasmas largely as a mechanism that proceeds by chemical action (i.e. the reaction of Si by F-atoms generated by the plasma to form  $\text{SiF}_4$ ). If etching action is purely chemical, however, the removal of material is isotropic, and no advantage in dimensional control is gained over wet etching (Chap. 15). In such processes, the plasma plays no role other than to produce